A direct method to calculate tip–sample forces from frequency shifts in frequency-modulation atomic force microscopy

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Citation: Applied Physics Letters **78**, 123 (2001); doi: 10.1063/1.1335546
View online: http://dx.doi.org/10.1063/1.1335546
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/78/1?ver=pdfcov
Published by the AIP Publishing

A direct method to calculate tip–sample forces from frequency shifts in frequency-modulation atomic force microscopy

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(Received 6 September 2000; accepted for publication 27 October 2000)

Frequency-modulation atomic force microscopy (FMAFM) has proven to be a powerful method for imaging surfaces with true atomic resolution. However, the tip–sample forces are not directly accessible by FMAFM. Here, an algorithm to recover the tip–sample forces from the frequency shift curve is introduced and demonstrated with experimental data. Also, an intuititive connection between frequency shift Δf and tip–sample force gradient k_{ts} that simplifies the calculation of FMAFM images is established: Δf is a convolution of k_{ts} with a semispherical weight function. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1335546]

In atomic force microscopy (AFM),[1] the frequency-modulation (FM) technique[2] is very powerful for imaging surfaces in vacuum with true atomic resolution.[3] Force spectroscopy, that is the measurement of the tip–sample potential V_{ts} and its derivatives with respect to vertical distance z (force $F_{ts}=\partial V_{ts}/\partial z$ and force gradient $k_{ts}=\partial F_{ts}/\partial z$) is a tremendous experimental challenge in quasistatic AFM but the interpretation of the results is straightforward.[4] In FMAFM, some of the experimental challenges (jump to contact, etc.) are not present, but the interpretation of the data is more difficult, because frequency shifts rather that forces or force gradients are measured. In an attempt to determine V_{ts} by FMAFM, analytic expressions for frequency shift versus distance curves $\Delta f(z)$ were fitted to the experimental data and the forces were recovered from the corresponding $F_{ts}(z)$ expressions.[5] Using this method, the forces between a silicon tip and a Si(111)–(7×7) surface were determined above adatom sites and cornerholes recently by Lantz *et al.*[6] However, in general, it is not possible to fit an experimental frequency shift curve with a single analytic expression for the whole distance range of interest. A direct way for recovering $V_{ts}(z)$ from $\Delta f(z)$ is therefore needed. A numerical method to reconstruct $F_{ts}(z)$ from $\Delta f(z)$ has been introduced by Gotsmann *et al.*[7] Dürig[8] and Hölscher *et al.*[9] have proposed semianalytical algorithms to deconvolute $V_{ts}(z)$ and its derivatives from $\Delta f(z)$ directly. While the numerical method works for small and large amplitudes, the semianalytic methods are suited best for amplitudes which are large compared to the range of the tip-sample forces. Since it has been demonstrated theoretically[10] and experimentally,[11,12] that minimal noise is obtained by using amplitudes which are in the order of the range of the tip–sample potential, a method to deconvolute $F_{ts}(z)$ from $\Delta f(z)$ for small amplitudes is highly desirable. Recently, Dürig introduced a method which works well for small amplitudes.[13] However, in this method the amplitudes and phases of the higher harmonics of the cantilever motion have to be known. For cases where the frequency spectrum of the cantilever is not available, an algorithm is presented here which allows the deconvolution of $V_{ts}(z)$ from a frequency shift curve $\Delta f(z)$.

In FMAFM, a cantilever with spring constant k is subject to positive feedback such that it oscillates with a constant amplitude A. When the oscillating cantilever is brought close to a sample, its oscillation frequency changes from its eigenfrequency f_0 to $f=f_0+\Delta f$ due to the force gradient k_{ts} between the tip of the cantilever and the sample. When the gradient of the tip-sample forces k_{ts} is constant for the whole z range of the tip motion, the frequency shift is given by[2]

$$\Delta f=f_0\frac{1}{2k}k_{ts}. \tag{1}$$

If k_{ts} is not constant during a cycle, Δf can be calculated by first order perturbation theory using the Hamilton–Jacobi approach[5]

$$\Delta f(z_b)=\frac{f_0^2}{kA}\int_0^{1/f_0}F_{ts}(z_b+A\cos(2\pi f_0 t))\cos(2\pi f_0 t)dt, \tag{2}$$

where z_b is the vertical base position of the cantilever as shown in Fig. 1 (the sign of the right hand side of Eq. (2) is opposite to the respective equation in Ref. 5 because the z axes are also reversed). This formula has been confirmed by several authors.[14–19] The precision of Δf obtained by first order perturbation theory is determined by the ratio between

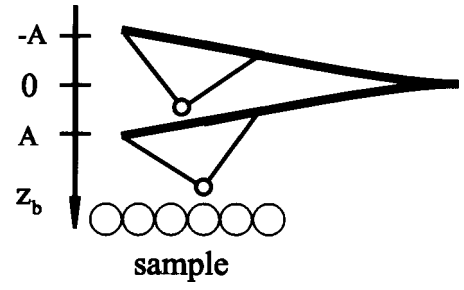

FIG. 1. Geometric situation at the derivation of a frequency shift curve and definition of z axis: an oscillating cantilever with amplitude A is approached to a sample, while the frequency shift Δf is recorded as a function of the position of the base of the cantilever z_b.

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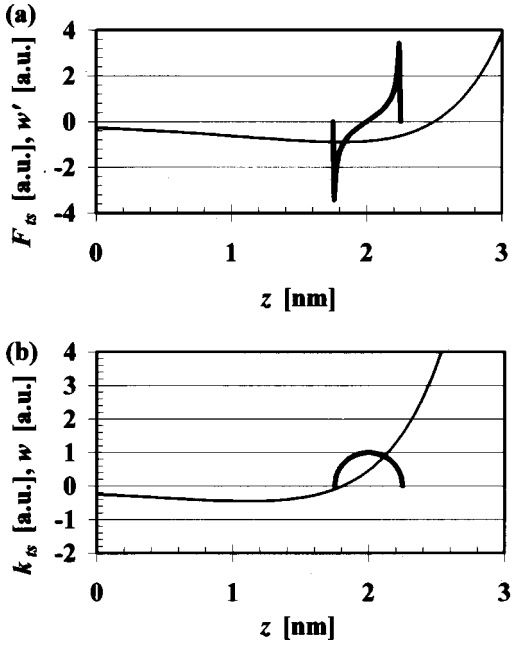

FIG. 2. Tip–sample forces F_{ts}, force gradient k_{ts}, weight functions w', and w as a function of z. The frequency shift Δf can be calculated by two methods: (a) convolution of tip–sample force $F_{ts}(z)$ with weight function w' or (b) convolution of force gradient $k_{ts}(z)$ with weight function w (semicircle with radius A).

the magnitude of the perturbation (i.e., the tip–sample potential V_{ts}) and the energy E of the oscillating cantilever. This ratio is in the order of 10^{-3} both in classical FMAFM with soft cantilevers and large amplitudes ($k \approx 20$ N/m, $A \approx 10$ nm) as well as in noncontact AFM with very stiff cantilevers and small amplitudes ($k \approx 2000$ N/m, $A \approx 1$ nm). In both cases, the energy $E = kA^2/2$ of the cantilever is ≈ 6 keV while the magnitude of V_{ts} does not exceed a few electron volts, at least for the cases where atomic resolution is desired and the interaction between tip and sample is dominated by the front atom of the tip.

Substituting $q' = -A\cos(2\pi f_0 t)$ in Eq. (2) yields

$$\Delta f(z_b) = -\frac{f_0}{2k}\frac{2}{\pi A^2}\int_{-A}^{A}\frac{F_{ts}(z_b - q')q'}{\sqrt{A^2 - q'^2}}\,dq'. \tag{3}$$

A display of the factors of the integrand F_{ts} and $w'(q',A) = q'/\sqrt{A^2 - q'^2}$ is shown in Fig. 2(a).

Equation (3) can be expressed in a more intuitive way through integration by parts

$$\Delta f(z_b) = \frac{f_0}{2k}\frac{2}{\pi A^2}\int_{-A}^{A} k_{ts}(z_b - q')\sqrt{A^2 - q'^2}\,dq'. \tag{4}$$

This expression is closely related to Eq. (1): the constant k_{ts} of Eq. (1) is replaced by a weighted average k_{ts}, where the weight function $w(q',A)$ is a semicircle with radius A divided by the area of the semicircle $\Gamma = \pi A^2/2$ [see Fig. 2 (b)]. For $A \to 0$, $w(q',A)$ is a representation of Dirac's delta function and Eq. (4) yields the same result as Eq. (1).

In a real experiment, the frequency shift curve $\Delta f(z_b)$ is not available as a continuous function, but as a set of N discrete points $\Delta f_i = \Delta f(z_i)$ where $z_i = (i-1)\Delta + z_1$ and $i \in [1,N]$. The vertical position z_1 denotes the first z value where Δf is nonzero, i.e., $\Delta f(z_1) \neq 0$ and $\Delta f(z) = 0$ for $z < z_1$. Thus, Eq. (3) can be written as a linear equation

$$\begin{pmatrix} \Delta f_1 \\ \Delta f_2 \\ \dots \\ \Delta f_N \end{pmatrix} = \begin{pmatrix} w'_{11} & 0 & \dots & 0 \\ w'_{21} & w'_{22} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ w'_{N1} & w'_{N2} & \dots & w'_{NN} \end{pmatrix} \begin{pmatrix} F_{ts1} \\ F_{ts2} \\ \dots \\ F_{tsN} \end{pmatrix}. \tag{5}$$

The elements of the matrix $\mathbf{W}' = (w'_{ij})$ are given by

$$w'_{ij} = \begin{cases} f_0 \dfrac{1}{2k}\dfrac{2}{\pi A}\displaystyle\int_{1-[2(i-j)]/[(2\alpha+1)]}^{1-[2(i-j+1)]/[(2\alpha+1)]} (\tau/\sqrt{1-\tau^2})\,d\tau \\ \qquad \text{for } 0 \leqslant i-j \leqslant 2\alpha \\ 0 \quad \text{else} \end{cases}, \tag{6}$$

where α is an integer expressing the amplitude A in terms of the step width Δ [$\alpha =$ round(A/Δ)] and $F_{tsi} = F_{ts}(z_{i+\alpha})$. Multiplication from the left with the inverse matrix $\mathbf{W}'^{-1} = (w'^{-1}_{ij})$ yields

$$\begin{pmatrix} F_{ts1} \\ F_{ts2} \\ \dots \\ F_{tsN} \end{pmatrix} = \begin{pmatrix} w'^{-1}_{11} & 0 & \dots & 0 \\ w'^{-1}_{21} & w'^{-1}_{22} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ w'^{-1}_{N1} & w'^{-1}_{N2} & \dots & w'^{-1}_{NN} \end{pmatrix} \begin{pmatrix} \Delta f_1 \\ \Delta f_2 \\ \dots \\ \Delta f_N \end{pmatrix}. \tag{7}$$

In principle, this deconvolution process can also be applied to k_{ts} via the inversion of $\mathbf{W}$, where $\mathbf{W} = (w_{ij})$ is created from $w(q',A)$ analogous to Eq. (6). Because of the analytic properties of $w(q',A)$, the convolution of k_{ts} with $w(q',A)$ is a smoothing operation, thus the deconvolution is roughening. Any noise present in the Δf data is greatly amplified by the deconvolution. For this reason, the experimental frequency shift curve has to be smoothened first before it can be used to recover k_{ts}. This effect is less dramatic in the convolution of F_{ts} and w', and it is preferable to deconvolute F_{ts} using w'.

Figure 3(a) shows experimental data derived with a tungsten tip on a KCl(100) surface (see figure caption for parameters). A z interval with a width of 3 nm has been divided into 120 points with a spacing of $\Delta = 25$ pm. A was 150 pm in this data set, thus $\alpha = 6$. The matrix elements w'_{ij} have been calculated according to Eq. (6). Inversion of $\mathbf{W}'$ (a 120×120 matrix) takes 6.2 s with a MAPLE V RELEASE 5 mathematics software[20] and a 450 MHz Intel Pentium computer. Figures 3(b) and 3(c) show the corresponding force F_{ts} and potential V_{ts}. The dots in Fig. 3(c) are Gordon and Kims calculated diatomic energy data for K^+ and Cl^- ions.[21] The experimental value for the bonding energy between tip and sample is -0.4 aJ ≈ -2.5 eV which compares well to Gordon and Kims data. The attractive energy in ionic crystals is mainly due to electrostatic interactions. In our experimental case, a tungsten tip was approached to the KCl surface. Assuming, that the metallic tip creates image charges of the surface, it is conceivable that the bonding energy of a sharp tip should be comparable to the case of the ionic species. However, there is a prominent deviation between theory and experiment: the experimental energy minimum is much wider than the theoretical minimum [see Fig. 3(c)]. This dis-

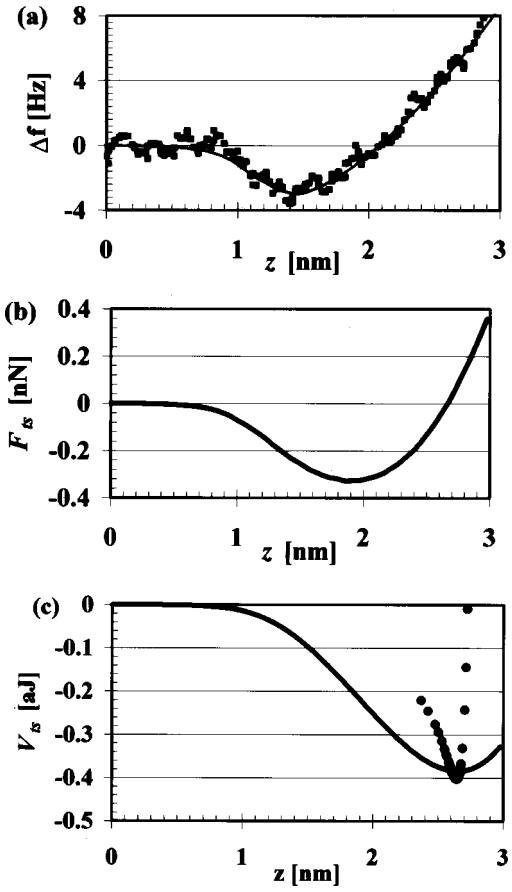

FIG. 3. (a) Experimental data of $\Delta f(z)$ (squares) for a tungsten tip and a KCl sample, recorded with an amplitude of $A=0.15$ nm, a spring constant of $k=1800$ N/m and $f_0=25\,068.4$ Hz. The solid line is a smoothened curve used for the deconvolution; (b) tip–sample force $F_{ts}(z)$ corresponding to the $\Delta f(z)$ data in (a); (c) solid line: tip–sample potential $V_{ts}(z)$, derived by integration of (b), dots: calculated diatomic energy data for K^+ and Cl^- ions (after Gordon and Kim).

crepancy has been observed and discussed before by Jarvis *et al.*[4] and is most likely due to elastic deformations of tip and sample.

As mentioned above, the deconvolution method is limited to weak perturbations. In this case, the relative frequency shift $\Delta f/f_0$ is small and the cantilever motion is almost perfectly sinusoidal — the amplitude A_n of the nth harmonic is approximately given by:[8]

$$A_n=-A\frac{\Delta f}{f_0}\frac{2}{1-n^2}.$$

The error in the deconvolution of F_{ts} from Δf caused by neglecting the higher harmonics of the cantilever motion is thus estimated to be of the order of $\Delta f/f_0$. Other sources of error are rooted in the discretization of the z axis — the stepwidth Δ has to be choosen small enough such that further decreasing it does not alter (F_{tsi}) significantly.

In summary, a method to obtain the tip–sample potential from frequency shift data has been introduced and demonstrated, and an intuitive connection between frequency shift and tip–sample potential has been derived which might be useful both for understanding frequency shift data analyzing tip sample forces and calculating images.

The author wishes to thank U. Dürig for discussions and J. Mannhart for support and editorial advice. This work is supported by BMBF Grant No. 13N6918/1.

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